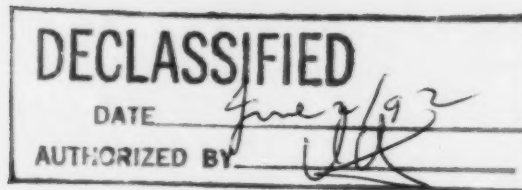


PROTECTED BUSINESS INFORMATION



**TESTING OF RECYCLABLE MATERIALS FOR
INDUSTRY, SCIENCE AND TECHNOLOGY CANADA**

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Analytical Methodology**

MICROMEDIA

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la technologie des minéraux et de
l'énergie (CANMET).

Protected Business Information**INTRODUCTION**

CANMET Chemical Laboratory has received a cost recovery contract from Industry, Science and Technology Canada for the leaching and chemical analysis of fourteen samples of recyclable materials originating from the Canadian mineral processing and metals industries. The work is part of an investigation being conducted by ISTC, Environment Canada, and EMR Mineral Policy Sector.

The contract requires the application of a CGSB Standard mandated under the Transport of Dangerous Goods Act, which was originally designed to regulate solid waste materials, to typical recyclable materials from Canadian industries.

This report describes the results obtained upon applying the standard to these materials, together with relevant comments. Also included is a brief outline of issues important to the sampling of heterogeneous materials.

BACKGROUND

Recyclable materials are by-products of processing and fabrication in the mineral processing and metals industries, and are destined for further processing, often at a site other than the place of origin. Their trade in Canada and internationally has significant economic impact.

CGSB Standard 164-GP-IMP has been adopted to regulate the transport of recyclable materials to and from processors in these industries. This standard was originally designed to regulate solid waste materials destined for transport to and disposal in a landfill site.

Canadian recycling industries have expressed concerns that this standard may be unsuitable for recyclable materials, because it was designed for quite another purpose.

The present investigation is to gather more information on this matter.

SAMPLE DESCRIPTION

Some 26 samples of varying recyclable materials have been collected from Canadian industries by Ms. E. Koren of MPS. In quantity they ranged from 100 grams to several kilograms weight.

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In appearance, the samples ranged from homogeneous powders of various colours, to powders mixed with lumps, metallic pieces, heterogeneous metallic scrap, and large metallic chunks.

Most samples were dry as received; however, four samples were fine powders that were wet with water.

The sample materials, appearances, and total weights received, are shown in Table 1, along with a sample number arbitrarily assigned.

SAMPLE SPLITTING

As requested by MPS, most samples were split into two half portions. This was done with a sample riffler of appropriate size, or manually by the cone-and-quarter method.

One half split of each sample was returned to MPS to be sent to DOE Laboratories for further testing.

The method used for sample splitting is shown in Table 2.

SAMPLE SIZING

The remaining half split of each sample, was in most cases divided into 2 size fractions, using the sieve size of 9.5 mm as specified. (Actual sieve size 9.423 mm, i.e., 0.371 in.).

The electronic devices were not screened because of the widely varying material present, which included transistors, and tangled chunks of fine wire.

Screening of the wet samples was not attempted.

The auto catalyst sample was not screened, as it appeared to be all much smaller than 9.5 mm.

The method used for sample sizing, and the size distribution, is shown in Table 2.

OUTLINE OF CGSB STANDARD

The main features of CGSB Standard 164-GP-IMP are summarized below; the complete text appears in Annex 1.

- vacuum filtration to separate liquid and solid phases

TABLE 1. Sample Description

Sample Number	Material	Description	Total Weight Received
01	Lead Dross	yellow, granular, some lumps	2.32 Kg
02	Lead Dross	black, fine grain, some small lumps	627 g
03	Lead Skimming	silver coloured lumps	600 g
04	Zinc Dross	grey, granular, small lumps	1.54 Kg
05	Lead Skimming	grey, large cut pieces 1½" to 2"	1.74 Kg
06	Calcined Catalyst	grey, granular	3.54 Kg
07	Petroleum Catalyst	black, small grains	4.21 Kg
08	Metallic Turnings	dirty silver colour, fine powder to chunks	3.52 Kg
09	Plating Hydroxide	wet sample; green, clay-like	3.96 Kg
10	Grindings	wet sample; grey-black, fine easily-crushed lumps	2.40 Kg
11	Shredded Circuit Boards	copper, laminated plastic; size ¼" to greater than 1"	71 g
12	Ashes	black, powder with small lumps	148 g
13	Copper Wires	varying lengths and insulation types	96 g
14	Slag	black, powder with large lumps	590 g
15	Shredded Electronics	silver and copper colour; fine wires, small metal flakes	981 g
16	Electronic Devices	2 packs: (a) transistors (b) powder, pieces of circuit boards, fine tangled copper wire	197 g
17	Coppercake	wet sample; grey-black, powder with large lumps	1.55 Kg

TABLE 1. Sample Description (continued)

Sample Number	Material	Description	Total Weight Received
18	Plating Sludge	wet sample; dark green-black, powder	1.56 Kg
19	Copper Arsenical Slimes	light green, powder with lumps	2.30 Kg
20	Die Cast Skimming	2 packs: silver metal, lumps $\frac{1}{4}$ " to 3"	1.40 Kg
21	Pure Zinc	silver metal, wafers 2" x 2" x $\frac{1}{2}$ "	1.21 Kg
22	Pure Lead	silver metal, one wedge 4" x 2" x 1"	1.07 Kg
23	Lead	grey-silver metal, cut pieces 2" x 2" x 1" to 1" x 1" x $\frac{1}{2}$ "	1.13 Kg
24	Die Cast	silver metal, 2 pieces 3" x $\frac{3}{4}$ " x $\frac{3}{4}$ "	180 g
25	Die Cast Dross	grey metallic pieces, powder to $\frac{1}{2}$ "	430 g
26	Auto Catalyst Monolith	2 bottles; fine grey powder	~ 3 Kg

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TABLE 2. Sample Splitting and Sizing

Sample Number	Material	Splitting Method	Sizing Method	Percent of Sample <9.5 mm
01	Lead Dross	riffle	screen	96
02	Lead Dross	riffle	screen	98
03	Lead Skimming	riffle	screen	42
04	Zinc Dross	riffle	screen	96
05	Lead Skimming	manual	N/A	0
06	Calcined Catalyst	riffle	screen	99
07	Petroleum Catalyst	riffle	screen	100
08	Metallic Turnings	riffle	screen	91
09	Plating Hydroxide	wet sample: cone and quarter	N/A	unknown
10	Grindings	wet sample: cone and quarter	N/A	unknown
11	Shredded Circuit Boards	manual	N/A	unknown
12	Ashes	riffle	screen	89
13	Copper Wires	manual	N/A	unknown
14	Slag	riffle	screen	75
15	Shredded Electronics	riffle	screen	100
16	Electronic Devices	manual	N/A	unknown

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TABLE 2. Sample Splitting and Sizing (concluded)

Sample Number	Material	Splitting Method	Sizing Method	Percent of Sample <9.5 mm
17	Coppercake	wet sample; dried by error; riffle	screen	74
18	Plating Sludge			
19	Copper Arsenical Slimes	wet sample: cone and quarter riffle	N/A	unknown
20	Die Cast Skimming		screen	69
21	Pure Zinc	2 packs received: not split	N/A	unknown
22	Pure Lead	not split	N/A	
23	Lead	single piece: not split	N/A	0
24	Die Cast	not split	N/A	0
25	Die Cast Dross	2 pieces received: not split	N/A	0
26	Auto Catalyst Monolith	riffle	N/A	0
		2 bottles received: not split	screen	95
			none	visually, 100

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- screening through a 9.5 mm sieve
- extraction of the <9.5 mm portion by rotating in dilute acetic acid for specified times, with monitoring and adjustment of pH
- chemical analysis of extraction leachate for constituents of interest

APPLICATION OF CGSB STANDARD FOR THIS CONTRACT

For the application of this standard to the recyclable materials supplied, the following technical conditions were agreed for this contract.

1. Determinations of moisture content, and structural integrity tests, are judged unnecessary for these samples; samples to be prepared and analyzed on "as-received" basis.
2. Samples to be split into two portions; one retained by MSL for analysis, the other to be sent to DOE Wastewater Technologies Laboratories in Burlington.
3. Samples to be screened using 9.5 mm sieve. Only the <9.5 mm portion to be analyzed.
4. Of the original 26 samples received for splitting and sizing, Ms. Koren will select 14 samples to undergo extraction and chemical analysis.
5. The 14 samples to be extracted according to 164-GP-IMP with pH monitoring and adjustment. The sample size and leachate volume will be scaled down by half, to 25 g/500 mL.
6. Chemical analysis of leachates:

As, Ba, Cd, Cr, Pb, Se, Ag
Hg

by ICP
by VGAAS

It was discovered after delivery that four of the samples were wet. This prevented mechanical splitting of the sample; instead, a manual cone and quarter procedure was used. The wet condition also prevented screening of the samples; however, it appeared that the particle sizes of these samples were all <9.5 mm.

It was agreed that a portion of the wet samples would be dried to constant weight at 60°C as stipulated in the standard, and the resulting moisture content be used to calculate the weight of sample required for the extraction. This was done for three of the samples. Unfortunately the fourth sample (17,

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weight of sample required for the extraction. This was done for three of the samples. Unfortunately the fourth sample (17, Coppercake) was inadvertently dried at 105°C; it was then decided to proceed with the analysis as if this were a dry sample.

MOISTURE DETERMINATION

As described above, the three wet samples were dried at 60°C to constant weight. The resulting moisture value was used to calculate the amount of wet sample to be taken for leaching, to give the equivalent of 25 g dry sample.

The results appear in Table 3.

TABLE 3. Moisture

Sample	% Moisture at 60°C; 5 g sample				Weight Required for 25 g Dry Sample
	4 hrs	23 hrs	30 hrs	43 hrs	
09 Plating Hydroxide	69.3	72.5	72.5	72.5	90.9 g
10 Grindings	19.9	19.9	19.9	19.9	31.2 g
18 Plating Sludge	60.7	71.1	71.1	71.1	86.5 g

SAMPLE EXTRACTION

As agreed, the fourteen sample materials were extracted, following 164-GP-IMP as closely as possible. In addition, two blank determinations were carried through the extraction procedure.

Duplicate 25 g portions of each material were taken, and extracted under the prescribed pH and time conditions; the final extract volume was 500 mL. This is equivalent to the ratio of 50 g sample in 1000 mL volume described in the standard. Under this condition, the maximum volume of acetic acid to be added is 100 mL. All extractions were conducted in 500 mL Erlenmeyer flasks capped with a rubber stopper.

Unfortunately, a rotator similar to the one described in the standard was not available in-house, and could not be borrowed

from outside laboratories. Therefore the samples were extracted on a device which rotated two samples at a time through 360° on a central axis. The speed of rotation which could not be varied was 60 rpm, rather than the 10 rpm specified in the standard.

For each sample extracted, a record of the pH and volume of acetic acid added at various times during the extraction appears in Table 4.

Observations

- a) The pH meter response is very slow. This is probably due to a combination of the high level of suspended solids, and to the leach solution being highly buffered with dissolved salts.
- b) Section 7.2.11 of the Standard is somewhat ambiguous. It is not clear whether a final pH adjustment is required after 24 hours, or simply a reading of the pH at this time. In the present test work, the pH was adjusted at this time.
- c) During the extraction, Samples 04 Zinc Dross and 25 Die Cast Dross reacted with the extraction medium to produce a gas, which increased the pressure in the extraction flask to cause a very small leakage (approximately 20 mL) of leachate past the rubber stopper. This gas is probably hydrogen, formed by the decomposition of metal by acid.

CHEMICAL ANALYSIS

Chemical analysis was conducted on each of the extraction leachates obtained. In addition, a second independent analysis was obtained from extraction leachate A of each sample material. The two blank determinations were also analyzed.

An outline of the analytical methods used is shown below. Also shown are measures used to verify the results.

The analytical results are shown in Table 5. The Concentration Limit (CL) for each element, as taken directly from the Standard, is also given in the Table.

As, Ba, Cd, Cr, Pb, Se, Ag

The above elements were determined by inductively coupled plasma atomic emission spectroscopy. For most elements a Jobin-Yvon Model 38 spectrometer was used; for silver and barium, a Thermo Jarrell-Ash Model 2400 spectrometer was used. The 2400 was also used for a preliminary survey of the sample solutions for the elements of interest, and possible interferences.

TABLE 4. Monitoring of Extractions

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Sample	Sample Weight g	15 minutes		1 hour		3 hours		6 hours		22 hours		24 hours		Final pH	Total Acid Added mL
		pH	mL Acid	pH	mL Acid	pH	mL Acid	pH	mL Acid	pH	mL Acid	pH	mL Acid		
01 Lead Dross	A 25.00	12.5	100.0	10.0	--	10.8	--	11.2	--	12.1	--	12.1	--	12.1	100.0
	B 25.00	12.5	100.0	9.6	--	10.5	--	11.1	--	12.1	--	12.1	--	12.1	100.0
03 Lead Skimming	A 25.00	10.3	4.25	7.5	8.20	7.5	20.0	6.7	13.95	5.8	10.3	5.3	6.5	5.0	63.2
	B 25.01	10.3	3.40	7.5	6.40	7.5	18.5	6.8	13.8	6.6	13.9	5.3	7.5	5.0	63.5
04 Zinc Dross	A 25.00	7.2	6.00	7.0	8.20	7.1	13.3	6.6	14.0	7.0	41.0	6.0	17.5	5.2	100.0
	B 25.00	7.1	6.00	7.0	8.50	7.0	16.4	6.6	15.5	6.7	44.1	5.9	9.5	5.4	100.0
07 Petroleum Catalyst	A 25.00	5.5	0.30	5.6	0.40	5.6	0.6	5.4	0.5	5.5	1.0	5.2	0.3	5.0	3.1
	B 25.00	5.5	0.25	5.6	0.45	5.6	0.6	5.5	0.7	5.5	0.8	5.2	0.5	5.0	3.3
08 Metallic Turnings	A 25.00	8.0	0.9	6.6	0.9	5.9	1.2	5.4	0.5	6.1	1.9	5.4	1.1	5.0	6.5
	B 25.00	8.0	0.8	6.6	1.0	5.5	0.8	5.7	1.3	6.8	3.6	5.5	2.1	5.0	9.6
09 Plating Hydroxide	A 90.90 Wet	10.0	100.0	6.1	--	6.5	--	6.6	--	6.7	--	6.7	--	6.7	100.0
10 Grindings	B 90.90	10.0	100.0	6.1	--	6.5	--	6.6	--	6.7	--	6.8	--	6.8	100.0
	A 31.20 Wet	7.5	4.5	4.7	--	5.1	0.1	5.1	0.4	5.0	--	5.0	--	5.0	5.0
15 Shredded Electronics	B 31.20	7.6	3.5	4.8	--	5.4	0.9	5.3	0.7	5.1	0.1	5.1	0.1	5.0	5.3
	A 25.00	6.5	0.3	6.0	0.2	6.1	0.4	6.3	0.7	7.0	1.3	6.1	1.2	5.0	4.1
16 Electronic Devices	B 25.00	6.5	0.2	6.0	0.3	6.2	0.4	6.2	0.5	7.1	1.3	6.1	1.0	5.0	3.7
	A 25.00	8.0	0.5	6.8	0.7	6.8	1.0	6.7	1.5	6.6	1.5	5.7	--	5.7	5.2
17 Coppercake	B 25.00	7.8	0.5	6.6	0.7	6.6	0.9	6.4	1.4	6.4	2.0	5.5	--	5.5	5.5
	A 25.00	7.0	31.5	6.4	68.5	6.0	--	5.9	--	6.1	--	6.2	--	6.2	100.0
	B 25.00	7.1	23.5	6.5	76.5	6.0	--	5.9	--	6.1	--	6.2	--	6.2	100.0

TABLE 4. Monitoring of Extractions (concluded)

Sample	Sample Weight g	15 minutes		1 hour		3 hours		6 hours		22 hours		24 hours		Final pH	Total Acid Added mL
		pH	mL Acid	pH	mL Acid	pH	mL Acid	pH	mL Acid	pH	mL Acid	pH	mL Acid		
18 Plating	A 86.50	8.5	50.0	5.5	20.0	5.5	23.0	5.3	7.0	5.4	--	5.4	--	5.4	100.0
	Wet														
Sludge	B 86.50	8.4	50.0	5.5	20.0	5.5	21.0	5.3	9.0	5.4	--	5.4	--	5.4	100.0
19 Copper	A 25.00	4.2	--	4.2	--	4.0	--	4.0	--	4.0	--	4.0	--	4.0	0
Arsenical	B 25.00	4.2	--	4.2	--	4.0	--	4.0	--	4.0	--	4.0	--	4.0	0
Slimes															
25 Die Cast	A 25.00	7.1	8.9	6.6	11.9	6.5	13.5	6.4	15.0	6.5	27.4	6.0	21.5	5.0	98.2
Dross	B 25.00	6.8	9.6	6.6	12.0	6.5	13.0	6.3	15.0	6.4	28.5	6.0	21.9	5.0	100.0
26 Auto	A 25.00	7.0	1.7	5.8	1.5	5.3	1.0	5.1	1.0	5.0	--	5.0	--	5.0	5.2
Catalyst	B 25.00	7.0	1.8	5.7	1.5	5.2	0.9	5.1	1.0	5.0	--	5.0	--	5.0	5.2
Monolith															

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The extraction leachates were analyzed as received. Samples containing high concentrations were diluted in 2% nitric acid. Background correction was used on all lines for the determination of low concentrations. The following analytical lines were used:

Ag	328.068 nm	As	193.696 nm
Ba	455.403	Cd	214.438
Cr	206.149, 267.716*	Pb	220.353
Se	196.026		

* The Cr 267.716 line was used for samples containing high concentrations of zinc, because of interference on the Cr 206.149 line.

Hg

Mercury was determined by vapour generation atomic absorption spectrometry, using a Varian Spectra AA-20 equipped with a VGA-76 vapour generation accessory. The wavelength was 253.7 nm.

Aliquots of the extraction leachates were oxidized by digestion with potassium dichromate, and nitric and hydrochloric acids. Standards were prepared in the identical fashion. Samples and standard solutions were aspirated into the VGA-76 and reduced with stannous chloride.

Quality Control

The precision of the complete analytical procedure, including sampling, extraction and determination, is indicated by the results from the duplicate extractions A and B of each sample material.

The precision of the analytical determinations alone is indicated by the results of the two independent analyses of extraction A of each material.

Reagent blank samples were carried through the complete procedure, and the usual performance checks were completed when calibrating the analytical instrumentation.

A verification of the accuracy of the results was not possible because no certified reference materials of similar samples were available at the time the work was done.

As an additional check on accuracy and precision, a number of extraction leachates will be exchanged by CANMET and Wastewater Technologies Laboratories, and analyzed for the elements of interest. Time did not permit this to be done for inclusion in the present report; the results of the exchange will appear later as an Addendum.

TABLE 5. Chemical Analysis of Extracts

Sample Material	Leachate	As CL mg/L	Ba CL mg/L	Cd CL mg/L	Cr CL mg/L	Pb CL mg/L	Se CL mg/L	Ag CL mg/L	Hg CL μg/L
01 Lead Dross	A	1.4	<1.0	<0.003	<0.007	53	<0.07	<0.01	0.04
	A	1.5	<1.0	0.004	<0.007	55	<0.07	<0.01	0.06
03 Lead Skimming	B	0.12	<0.1	<0.003	<0.007	209	<0.07	<0.01	0.02
	A	<0.03	<1.0	0.004	<0.007	5346	<0.07	<0.01	0.01
	A	<0.03	<1.0	0.003	<0.007	5456	<0.07	<0.01	0.05
	B	<0.03	<1.0	<0.003	<0.007	5451	<0.07	<0.01	0.03
04 Zinc Dross	A	<0.03	<1.0	0.008	0.013	1.5	<0.07	<0.01	0.02
	A	<0.03	<1.0	0.009	0.019	1.1	<0.07	<0.01	0.05
	B	<0.03	<1.0	0.010	0.013	0.55	<0.07	<0.01	0.10
07 Petroleum Catalyst	A	1.4	<1.0	0.013	0.095	<0.06	<0.07	<0.01	0.04
	A	1.6	<1.0	0.013	0.108	<0.06	<0.07	<0.01	0.06
	B	1.4	<1.0	0.013	0.082	<0.06	<0.07	<0.01	0.03
08 Metallic Turnings	A	<0.03	<1.0	0.003	<0.007	0.27	<0.07	<0.01	0.02
	A	<0.03	<1.0	0.008	<0.007	0.26	<0.07	<0.01	0.05
	B	<0.03	<1.0	0.011	<0.007	0.09	<0.07	<0.01	0.02
09 Plating Hydroxide	A	<0.03	<1.0	<0.003	0.028	0.113	<0.07	<0.01	0.24
	A	<0.03	<1.0	<0.003	0.028	0.091	<0.07	<0.01	0.27
	B	<0.03	<1.0	<0.003	0.019	0.094	<0.07	<0.01	0.14

Table 5. Chemical Analysis of Extracts (continued)

Sample Material	Leachate	As CL mg/L	Ba CL mg/L	Cd CL mg/L	Cr CL mg/L	Pb CL mg/L	Se CL mg/L	Ag CL mg/L	Hg CL μg/L
10 Grindings	A	<0.03	<1.0	<0.003	<0.007	<0.06	<0.07	<0.01	0.03
	A	<0.03	<1.0	<0.003	<0.007	<0.06	<0.07	<0.01	<0.01
	B	<0.03	<1.0	<0.003	0.008	0.063	<0.07	<0.01	0.05
15 Shredded Electronics	A	<0.03	<1.0	0.007	0.007	64	<0.07	<0.01	0.03
	A	<0.03	<1.0	0.004	0.008	67	<0.07	<0.01	<0.01
	B	<0.03	<1.0	0.055	<0.007	77	<0.07	<0.01	0.04
16 Electronic Devices	A	<0.03	<1.0	27	0.013	99	<0.07	<0.01	0.30
	A	<0.03	<1.0	29	0.016	101	<0.07	<0.01	0.29
	B	<0.03	<1.0	38	0.013	88	<0.07	<0.01	0.28
17 Coppercake	A	8.0	<1.0	1858	0.021	129	<0.07	<0.01	0.07
	A	8.0	<1.0	1828	0.019	125	<0.07	<0.01	0.16
	B	8.8	<1.0	1838	0.015	131	<0.07	<0.01	<0.01
18 Plating Sludge	A	1.7	<1.0	26	2.2	46	<0.07	<0.01	0.04
	A	1.7	<1.0	26	2.2	46	<0.07	<0.01	0.05
	B	2.1	<1.0	36	2.3	49	<0.07	<0.01	0.08
19 Copper Arsenical Slimes	A	146	<1.0	0.099	<0.007	<0.06	<0.07	0.019	0.08
	A	143	<1.0	0.093	<0.007	<0.06	<0.07	0.019	0.09
	B	163	<1.0	0.127	<0.007	0.10	<0.07	0.018	0.08

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Table 5. Chemical Analysis of Extracts (concluded)

Sample Material	Leachate	As		Ba		Cd		Cr		Pb		Se		Ag		Hg	
		CL	mg/L	CL	mg/L	CL	mg/L	CL	mg/L	CL	mg/L	CL	mg/L	CL	mg/L	CL	mg/L
25 Die Cast Dross	A	0.12		<1.0		0.008		0.027		0.07		<0.07		0.010		<0.01	
	A	0.18		<1.0		0.010		0.030		0.06		<0.07		0.024		0.05	
26 Auto Catalyst Monolith	B	0.03		<1.0		0.006		0.030		<0.06		<0.07		<0.01		0.02	
	A	<0.03		<1.0		0.010		<0.007		5.6		<0.07		<0.01		<0.01	
Blank	A	<0.03		<1.0		0.009		<0.007		5.9		<0.07		<0.01		<0.01	
	B	<0.03		<1.0		0.009		<0.007		5.9		<0.07		<0.01		<0.01	
	A	<0.03		<1.0		<0.003		<0.007		<0.06		<0.07		<0.01		0.005	
	A	<0.03		<1.0		<0.003		<0.007		<0.06		<0.07		<0.01		--	
	B	<0.03		<1.0		0.005		<0.007		<0.06		<0.07		<0.01		0.001	

DISCUSSION OF RESULTS

Application of the Standard

The most significant observation made is that many of the sample materials are visibly heterogeneous in particle size and particle appearance. It remains to be seen whether the sample split sent to DOE is identical to the split retained by CANMET.

Furthermore, it would be expected that duplicate 25 g portions from the same sample split would not be identical. However, a comparison of results from extractions A and B of each sample material shows that there are relatively few sample materials or elements where there is an appreciable difference. This indicates that the complete procedure, including sampling, extraction and determination, is relatively reproducible for these materials.

In addition, the duplicate analytical determinations on extraction A of each material are in most cases quite similar, indicating that the precision of the determinations is good.

Suitability of the Standard

The results in Table 5 show that 10 of the 14 sample materials are above the Concentration Limits of the Standard for one or more elements, giving a total of 19 individual elements that are above the CL. These are shown in Table 6.

It must be mentioned that it is not clear whether the recyclable materials must meet the CLs as given in the Standard, or whether they are allowed to be a factor of 10 times or 100 times higher. The Standard should be written to explicitly define this point. In the absence of such a definition, this report compares the results directly to the CLs as written in the Standard.

Table 6. Analytical Results Exceeding Concentration Limit

<u>Materials Exceeding CL</u>	<u>Elements Exceeding CL</u>
01 Lead Dross	As, Pb
03 Lead Skimming	Pb
04 Zinc Dross	Pb
07 Petroleum Catalyst	As
15 Shredded Electronics	Cd, Pb
16 Electronic Devices	Cd, Pb
17 Coppercake	As, Cd, Pb
18 Plating Sludge	As, Cd, Cr, Pb
19 Copper Arsenical Slimes	As, Cd
26 Auto Catalyst Monolith	Pb

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It is not surprising that so many of the sample materials are above the CL, since they all arise from industrial processes where the elements of environmental interest are present in major amounts, often of economic importance. Moreover, many of the elements occur in forms that are readily soluble in an extraction procedure.

An additional factor of importance is the question of sampling bulk shipments of these materials. The Standard (Section 5.1) is not specific on this, but refers to US EPA SW-846 which was written for waste materials. The sampling of large bulk shipments (for example rail cars and truckloads) of heterogeneous materials is not a simple matter. Some of the important issues of sampling are mentioned in the following Section.

SAMPLING OF BULK MATERIALS

The most important factor affecting the accuracy of sampling of a heterogeneous bulk material is the degree of heterogeneity with respect to its composition and its particle size. The more heterogeneous the material, the more difficult it is to obtain a representative sample, and the more increments are required to achieve precision. It may make economic sense to preclassify the material by size ranges before sampling. The costs of classifying, sample division and crushing should be taken into account.

Various points to be considered when sampling;

1. Purpose of sampling;

- use to be made of sample
- information required - average concentration, particle concentration, variability
- precision required

2. Nature of material;

Heterogeneity - composition
- particle size and form

Safety - powder, dust
- reactivity, combustibility, volatility
- concentration of toxic material
- effect on environment

There are a number of methods that may be used for sampling heterogeneous bulk materials; incremental sampling, cone and quartering, riffing, and auger sampling are examples.

The process of sampling is an iterative process. It is necessary to know the degree of heterogeneity of the material in order to be able to sample properly; on the other hand, a proper

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sample must be taken in order to determine the degree of heterogeneity of the material.

A number of reference books are available, as well as standards documents such as ISO 3081, 3082, 3083 and ASTM E 877. The sample method chosen will of course depend on the nature of the sample material itself; no one sampling method will apply to the whole range of recyclable materials.

 Canadian General Standards Board

CGSB

Office des normes générales du Canada

ONGC

Leachate Extraction Procedure

This provisional standard sets out the requirements for determining the leachate extraction from solid waste materials

164-GP-IMP
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Canada

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K1A 1G6

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Canadian General Standards Board
Office des normes générales du Canada



LEACHATE EXTRACTION PROCEDURE

This provisional standard has been published to meet an urgent requirement of the Ministry of Transport. It has not been approved by a technical committee nor ratified by the Minister's Advisory Council on CGSB.

It is intended that this standard will be formally approved and published as a bilingual National Standard of Canada in the near future.

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February 1987

CANADIAN GENERAL STANDARD BOARD

LEACHATE EXTRACTION PROCEDURE

1. SCOPE

- 1.1 This standard sets out the requirements for determining the leachate extraction from solid waste materials

2. APPLICABLE PUBLICATIONS

The following publications are applicable to this standard:

- 2.1 United States Environmental Protection Agency

EPA SW-846 Test Methods For Evaluating Solid Waste,
September 1986

- 2.2 American Society for Testing and Materials (ASTM)

D1193 Standard Specification for Reagent Water

- 2.3 Reference to the above publications is to the issues in effect as of the date of this standard, unless otherwise specified. For the source of these publications, see the Notes section.

3. APPARATUS

- 3.1 Sieve, 9.5 mm mesh opening, stainless steel or plastic material.

- 3.2 Stainless steel filtration unit, 142 mm diameter, minimum 1L capacity, capable of sustaining a pressure of 500 kPa, applied to the solution to be filtered.

- 3.3 Membrane filter, 142 mm diameter, 0.45 µm diameter pore size, made of synthetic organic material such as teflon, cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is compatible with the leachate to be filtered. Teflon is recommended for organic constituents.

- 3.4 Glass fibre prefilter, 124 mm diameter, 3 µm to 12 µm pore size range.

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- 3.5 Vacuum filtration unit, 90 mm diameter.
- 3.6 Membrane filter 90 mm diameter, 0.45 μ m diameter pore size, made of synthetic organic material such as teflon, cellulose acetate, cellulose nitrate, nylon or polycarbonate and which is compatible with the leachate to be filtered. Teflon is recommended for organic constituents.
- 3.7 Glass fibre filter 70 mm diameter, 3 μ m to 12 μ m pore size range.
- 3.8 Solid waste rotary extractor - a device that rotates the bottles end over end about a central axis through 360 °, with a speed of 10 rpm. The dimensions of the box will depend on the needs of each laboratory. See Figure 1.
- 3.9 Structural Integrity Tester with a 31.8 mm diameter hammer weighing 0.33 kilogram and having a free fall of 152.4 mm. See Figure 2.
- 3.10 pH meter, with a readability of 0.01 pH unit and accuracy of $\pm$ 0.1 pH units.
- 3.11 Cylindrical bottles, wide mouth, 1250 mL capacity, polyethylene or glass with lined cap for inorganic constituents; glass with Teflon-lined cap or Teflon bottles for organic constituents.

4. REAGENTS and MATERIALS

- 4.1 Acetic acid 0.5 N. Dilute 29.4 mL of concentrated acetic acid [American Chemical Society (ACS) reagent grade] to 1000 mL with reagent water.
- 4.2 Reagent water, Type IV in accordance with ASTM Specification D 1193 "Reagent Water". For organic parameters, the reagent water shall be free of any organic substances to be analyzed, Type I in accordance with ASTM Specification D 1193.
- 4.3 Nitric acid, 10% (v/v). Add 100 mL of concentrated nitric acid (ACS reagent grade) to 900 mL of reagent water.
- 4.4 Nitrogen gas, pre-purified, scrubbed through a molecular sieve.

5. SAMPLING

- 5.1 Collect a sufficient amount of sample to provide approximately 100 g of solid material, using techniques set out in US EPA SW-846 "Test Methods For Evaluating Solid Waste".

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6. PREPARATION of APPARATUS

- 6.1 All glassware and equipment that comes into contact with the sample shall be cleaned in the following way before each use.
- 6.2 Wash with a non-phosphate detergent solution.
- 6.3 Rinse twice with tap water.
- 6.4 Rinse twice with reagent water.
- 6.5 Wash with 10% nitric acid.
- 6.6 Rinse several times with reagent water.
- 6.7 Store bottles filled with 10% nitric acid, until ready to use.
- 6.8 Rinse several times with reagent water before use.
- 6.9 Rinse clean oven dried bottles with methylene chloride, followed by methanol, for organic constituents.

7. PROCEDURES**7.1 Separation Procedure**

- 7.1.1 If the sample contains a distinct liquid and a solid phase, separate it into its component phases using the following procedure.
- 7.1.2 Determine the dry mass of the solids in the sample at 60°C, using a well homogenised sample. Use this mass to determine the amount of material to be filtered.
- 7.1.3 Assemble the filtration unit with a filter bed consisting of a 0.45 µm pore size membrane filter and a coarse glass fibre pre-filter upstream of the membrane filter (per manufacturer's instructions).
- 7.1.4 Select one or more blank filters from each batch of filters. Filter 50 mL portions of reagent water through each test filter and analyze the filtrate for the analytical parameters of interest. Note the volume required to reduce the blank values to acceptable levels.
- 7.1.5 Wash each filter used in the leach procedure with at least this predetermined volume of water. Filter under pressure until no water flows through the filtrate outlet.
- 7.1.6 Remove the moist filter bed from the filtration unit and determine its mass to the nearest ± 0.01 g.

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- 7.1.7 Re-assemble the filtration unit, replacing the filter bed, as before.
- 7.1.8 Grind the sample with a mortar and pestle, to a size that will pass through the opening of the filtration unit (less than 9.5 mm).
- 7.1.9 Agitate the sample by hand and pour a representative fraction of the solid and liquid phases into the opening of the filtration unit. Filter a sufficient amount of the sample to provide at least 60 g of dry solid material.
- 7.1.10 Pressurize the reservoir very slowly with nitrogen gas by means of the regulating valve on the nitrogen gas cylinder, until liquid begins to flow freely from the filtrate outlet.
- 7.1.11 Increase the pressure step-wise in increments of 50 kPa to a maximum of 500 kPa, as the flow diminishes. Continue filtration until the liquid flow ceases or the pressurizing gas begins to exit from the filtrate outlet of the filter unit.
- 7.1.12 De-pressurize the filtration unit slowly using the release valve on the filtration unit. Remove and weigh the solid material together with the filter bed to ± 0.01 g. Record the mass of the solid material.
- 7.1.13 Measure and record the volume and pH of the liquid phase. Store the liquid at 4°C under nitrogen until required in 7.2.13.
- 7.1.14 Discard the solid portion if the mass is less than 0.5% (w/v) of the fraction taken. If not, carry out the extraction procedure in 7.2

Note: For mixtures containing coarse grained solids, where separation can be performed without imposing a 500 kPa differential pressure, a vacuum filtration unit with a filter bed as described in 7.1.3 may be used. Vacuum filtration must not be used if volatile organic compounds are to be analysed.

7.2 Extraction Procedure

- 7.2.1 Prepare a solid sample for extraction by crushing, cutting or grinding, to pass through a 9.5 mm mesh sieve. If the original sample contains both liquid and solid phases, use the solid material from 7.1.14. The structural integrity

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procedure in 7.3 should be used for monolithic wastes which are expected to maintain their structural integrity in a landfill, (e.g. some slags and treated solidified wastes).

Note: Do not allow the solid waste material to dry prior to the extraction procedure.

- 7.2.2 Determine the moisture content of the de-watered sample, by drying a suitable fraction to constant weight at 60°C in an oven. Discard the dried solid material.
- 7.2.3 Place the equivalent of 50 g dry mass of the de-watered undried material into a 1250 mL wide mouth cylindrical bottle. Use additional bottles, if a larger volume of leachate is required for the analysis.
- 7.2.4 Add 800 mL (less the moisture content of the sample in mL) of reagent water to the bottle.
- 7.2.5 Cap the bottle and agitate it in the rotary extractor for 15 minutes before measuring the pH.
- 7.2.6 Measure and record the pH of the solution in the bottle using a pH meter, calibrated with buffers at pH 7.00 and pH 4.00. The solution should be stirred during the pH measurement.
- 7.2.7 If the pH is less than 5.2, carry out the procedure comencing at 7.2.10.1.
- 7.2.8 Add a sufficient volume of 0.5N acetic acid if the pH is greater than 5.2 to bring the pH to 5.0 ± 0.2 .

Note: Maximum Amount of Acid: No more than 4 mL of 0.5N acetic acid per gram of dry mass of sample may be added during the entire procedure. If the pH is not lowered to 5.0 ± 0.2 with this amount, proceed with the extraction.
- 7.2.9 Cap the bottle and place it in the solid waste rotary extractor. Rotate the bottle and its contents at 10 rpm for 24 hours at room temperature (20°C to 25°C).
- 7.2.10 Monitor, and manually adjust the pH during the course of the extraction, if it is greater than 5.2. The following procedure should be carefully followed:
 - 7.2.10.1 Measure the pH of the solution after 1 hour, 3 hours and 6 hours from the starting time. If the pH is above 5.2, reduce it to 5.0 ± 0.2 by addition of 0.5N acetic acid. If the pH is below 5.0 ± 0.2 , do not make any adjustments.

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- 7.2.10.2 Adjust the volume of the solution to 1000 mL with reagent water, if the pH is below 4.8 after 6 hours.
- 7.2.10.3 Measure and reduce the pH to 5.0 ± 0.2 , if required, after 22 hours and continue the extraction for an additional 2 hours.
- 7.2.11 Add enough reagent water at the end of the extraction period so that the total volume of liquid is 1000 mL. Record the amount of acid added and the final pH of the solution.
- 7.2.12 Separate the material into its component liquid and solid phases as described under the Separation Procedure (7.1). Discard the solid portion.

Note: It may be necessary to centrifuge the suspension at high speed before filtration, for leachates containing very fine grained particles.

- 7.2.13 Calculate the amount of free liquid from 7.1.13 corresponding to 50 g of the dry solid material. Add this amount to the leachate from 7.2.12.

Note: If the analysis is not performed immediately, store separate fractions of the leachate at 4°C, after adding appropriate preservatives for the analytical parameters of interest (See "US EPA SW-846 "Test Methods For Evaluating Solid Waste").

- 7.2.14 Analyze the combined solutions from 7.2.13 using methods set out in US EPA SW-846 "Test Methods For Evaluating Solid Waste" and which are capable of detecting the contaminants listed in Annex A, that are likely to be present at the detection limits specified for each contaminant.

- 7.2.15 Report concentrations of contaminants in the combined leachate and the free liquid solution as mg/L.

- 7.2.16 Carry a blank sample through the entire procedure, using dilute acetic acid at pH 5.0 ± 0.2 .

7.3 Structural Integrity Procedure

- 7.3.1 This procedure may be required prior to extraction for some samples as indicated in 7.2.1. It may be omitted for wastes with known high structural integrity.

- 7.3.2 Fill the sample holder with the material to be tested. If the sample of the waste is a large monolithic block, cut a portion from the block measuring 33 mm in diameter by 71 mm in length. For a treated waste (e.g. solidified waste) samples may be cast in a form with the above dimensions for

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the purposes of conducting this test. In such cases, the waste should be allowed to cure for 30 days prior to further testing.

7.3.3 Place the sample holder in the structural integrity tester, then raise the hammer to its maximum height and allow it to fall. Repeat this procedure 14 times.

7.3.4 Remove the material from the sample holder, and perform the extraction procedure (7.2). If the sample has not disintegrated, it may be sectioned; alternatively use the entire sample (after weighing) and a sufficiently large bottle as the extraction vessel. The volume of reagent water to be initially added is 16 mL/g of dry sample mass. The maximum amount of 0.5N acetic acid to be added is 4 mL/g of dry sample mass. The final volume of the leachate should be 20 mL/g of dry sample mass.

8. NOTES

8.1 ASTM publications are available from The American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

8.2 United States Government publications are available from the Superintendent of Documents, US Government Printing Office, Washington DC 20402.

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ANNEX A TO CGSB ~~XX-GP-XXX~~

<u>Contaminant</u>	<u>Concentration (mg/L)</u>
2,4,5-TP / Silvex / 2-(2,4,5-Trichlorophenoxy) propionic acid	0.1
2,4-D	1.0
Aldrin + Dieldrin	0.007
✓ Arsenic	0.5
✓ Barium	10.0
Boron	50.0
✓ Cadmium	0.05
Carbaryl / 1-Naphthyl-N-methyl carbamate / Sevin	0.7
Chlordane	0.07
✓ Chromium	0.5
✓ Cyanide	2.0
DDT	0.3
Diazinon / Phosphordithioic acid, o,o-diethyl o-(2-isopropyl- 6-methyl-4-pyrimidinyl) ester	0.002
Endrin	0.002
Flouride	15.0
Heptachlor + Heptachlor epoxide	0.03
✓ Lead	0.5
Lindane	0.04
✓ Mercury	0.01
Methoxychlor / 1,1,1-Trichloro-2, 2-bis(p-methoxyphenyl) ethane	1.0
Methyl parathion	0.07

- A2 -

<u>Contaminant</u>	<u>Concentration (mg/L)</u>
Nitrate + Nitrite	100.0
Nitrilotriacetic acid	0.5
Nitrite	10.0
PCBs	0.03
Parathion	0.35
✓ Selenium	0.1
✓ Silver	0.5
Toxaphene	0.05
Trihalomethanes	3.5
Uranium	0.2